



Synthesis, Characterization and Electrochemical Sensing Property of CuO and Carbon Functionalized CuO Nanoparticles

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Copper oxide (CuO) and carbon functionalized copper oxide nanoparticles (c-CuO) had been successfully synthesized by simple thermal decomposition method. Copper oxide was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaOH and carbon functionalized CuO was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and starch. The physical microstructure and morphology of nanoparticles were characterized by X-ray diffraction and field emission scanning electron microscopy (FESEM). From the XRD observation, it is evident that the particle size of CuO was obtained as a nano size by this synthesis process and the FESEM image showed the morphology of both nanoparticles. The electrochemical performance of the CuO and carbon functionalized CuO was evaluated by cyclic voltammetry. The cyclic voltammogram shows c-CuO nanoparticles are more sensitive towards detection of uric acid when compared to CuO.

Keywords: CuO nanoparticles, Starch, Cyclic voltammetry, Uric acid.

INTRODUCTION

Semiconductor nanoparticles have been extensively studied from experimental and theoretical viewpoint, owing to their potential applications, consequent to their size dependent optical properties. Among all semiconductor nanoparticles, copper oxides (Cu_2O and CuO) are interesting material with many application in various fields such as solar cells, Li-ion battery systems (negative electrode material), superconductors, magnetic storage systems, gas sensor, photo thermal and photoconductive systems¹⁻⁴.

Copper oxides represent very useful reference systems for the study of complex cuprates, most of which show high superconductivity (T_c). In fact, the discovery of the superconducting mixed-valence copper oxides and the possible role of magnetic interactions which facilitate the high- T_c have intensified the interest in these binary oxides. Many cuprates during chemical substitutions tend to show phase separation and insulator-to-metal transition. As shown in the literature, the different levels of this transition are usually observed as an increase in the infrared absorption within the dielectric gap and the subsequent formation of the low-energy tail due to the itinerant carriers⁵. Cuprous oxide (Cu_2O) and cupric oxide (CuO) (cuprite and tenorite, respectively) are the two most important stoichiometric compounds in the copper-

oxygen (Cu-O) system. Both materials are intrinsic p-type semiconductors with narrow energy band gaps (2.1 eV for Cu_2O , 1.2 eV for CuO) and exhibit a variety of interesting properties that can be fully exploited in several fields. Due to its low-symmetry, CuO has been found to exhibit ferroelectric properties⁶. Moreover, the large but almost constant paramagnetic susceptibility at low temperature is attributable to the exchange interaction between Cu^{2+} ions *via* O^{2-} ions⁷. Bulk and nano-CuO is thus used in preparation of a wide range of organic-inorganic nanostructured composites that possess unique characteristics such as giant magnetoresistance, high thermal and electrical conductivities as well as high mechanical strength⁸. The ionicity of the Cu-O bonds increases CuO nanoparticles, which is evident in the change in the optical band gap resulting in a blue shift⁹. The most remarkable envisaged applications of CuO are in gas sensor¹⁰ and solar cells. Gas sensors and solar cells based on tenorite are of direct interest to our research. To produce those devices, nanocrystalline CuO structures have been synthesized by techniques such as sol-gel¹¹, molecular beam epitaxy¹², microemulsions¹³ and sputtering¹⁴.

This work deals with the synthesis of CuO nanoparticles by thermal decomposition method. The electrochemical sensing property of CuO and c-CuO was evaluated by cyclic voltammetry using uric acid as an analyte.

EXPERIMENTAL

The following chemicals were used to synthesize the CuO and c-CuO. Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) purchased from Qualigens, sodium hydroxide and starch from SRL. In this synthesis, analytical reagent grade chemicals were used and all the solutions were prepared with deionized water (double distilled). The CuO and c-CuO were characterized by various techniques such as X-ray diffraction analysis, field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDAX). The XRD spectra of the compounds were recorded on Rich Siefert 3000 diffractometer using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$).

The size, shape, morphology and elemental composition of CuO and c-CuO were characterized by field emission scanning electron microscopy (FESEM). The FESEM analysis was carried out on JOEL JEM-6360 scanning electron microscopy. The synthesized CuO nanoparticles were powder in nature. About 1 mg of powdered sample was dispersed in 3 mL of double distilled water by sonicating for 5 min. One drop of the dispersed sample solution was dropped on the aluminium stub (sample holder) using micropipette. Then it allowed to drying at room temperature for 3 h, and the dried sample was analyzed by FESEM.

Electrochemical instrument: The voltammetric determinations were performed on a CHI 600A coupled with personal computer for data acquisition and potential control. All the voltammograms were taken using a conventional three electrode system which consists of modified glassy carbon electrode as a working electrode, platinum wire as a counter electrode (auxiliary electrode) and saturated calomel electrode as reference electrode.

Synthesis of CuO nanoparticles: The synthesis of CuO nanoparticles has been achieved by thermal decomposition method. In typical synthesis 2.49 g copper sulphate and 0.08 g of sodium hydroxide was dissolved in 125 mL of double distilled water and stirred for 0.5 h. The reaction mixture was filtered and washed with double distilled water twice and dried. The dried precipitate was heated in a muffle furnace at 550°C for 3 h to get CuO nanoparticles.

Synthesis of c-CuO: 1 g of copper sulphate and 10 g of starch was dissolved in hot water and stirred for 1 h and evaporated to dryness on a hot plate. The dull blue precipitate was decomposed in muffle furnace at 550°C for 3 h to get c-CuO.

Modification of glassy carbon electrode¹⁵: The bare CuO and c-CuO were modified to the glassy carbon electrode by drop casting method. First, the glassy carbon electrode surface was smoothly polished using emery paper (grade no. 2). About 0.5 mg of powdered CuO nanoparticles were dispersed in 1 mL of double distilled water by sonicating for 5 min. $0.5 \mu\text{L}$ of the dispersed CuO nanoparticles solution was drop casted on the surface of the smoothly polished glassy carbon electrode using micropipette and allow drying at room temperature for 0.5 h. The same procedure adopted to c-CuO as well.

RESULTS AND DISCUSSION

X-ray diffraction method: Fig. 1 shows the XRD pattern of CuO, the diffraction peaks at $35, 39, 49, 54, 58, 62$ and 66°

are in accordance with standard XRD card of 48-1548. XRD data also revealed that the CuO obtained has monoclinic structure with space group of C_{2v} . There was no indication of any other additional phases, expect CuO in the XRD pattern. The particle size calculated from the Scherer's formula was found to be about 50 nm.

$$D = K\lambda/(\beta \cos \theta)$$

where, K is a constant (0.9), λ is the wavelength, β is the full width at the half-maximum of the line and θ is the diffraction angle.

Further, the lattice parameters of the hexagonal CuO was found to be $a = 4.68 \text{ \AA}$, $b = 3.42 \text{ \AA}$, $c = 5.13 \text{ \AA}$.

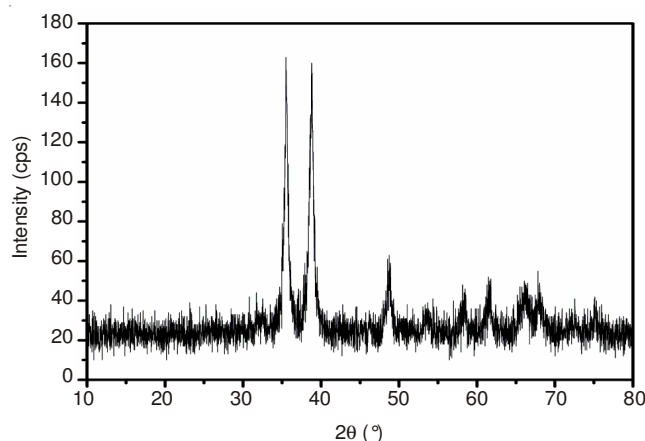


Fig. 1. XRD pattern of bare CuO nano particles

Fig. 2 shows the diffraction peaks at $35, 39, 49, 54, 58, 62$ and 66° in addition to these peaks there were some peaks which corresponds to that of carbon at $12, 31, 66$ and 75° . From the XRD analysis it is clear that the formation of CuO nanoparticles (Fig. 1) and in case of Fig. 2 the formation of CuO nanoparticles along with the carbon was observed. In case of c-CuO, the size of the particles found to be about 80 nm.

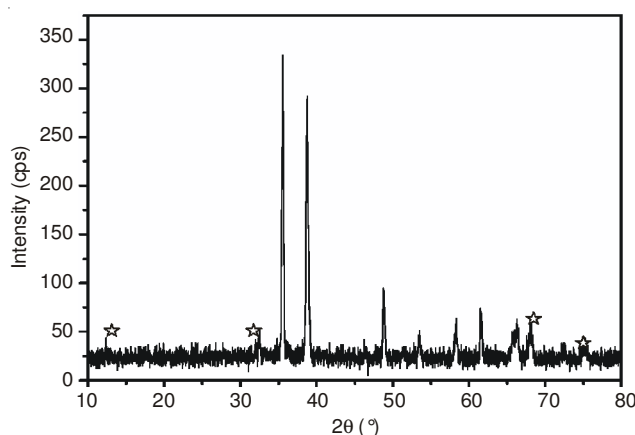


Fig. 2. XRD pattern of c-CuO (☆ Denotes the peaks of carbon)

Field emission scanning electron microscopy (FESEM): Field emission scanning electron microscopy studies were taken to determine the size, shape and morphology of CuO and c-CuO. Fig. 3 clearly shows the CuO nanoparticles has highly porous morphology of the surface. The dimension of

the particles were found to be in the nm range. The reason for the agglomeration is mainly due to the temperature at which the CuO nanoparticles synthesized. Fig. 3a,b shows the FESEM images of the CuO nanoparticles magnification of 2 and 10 μm , respectively.

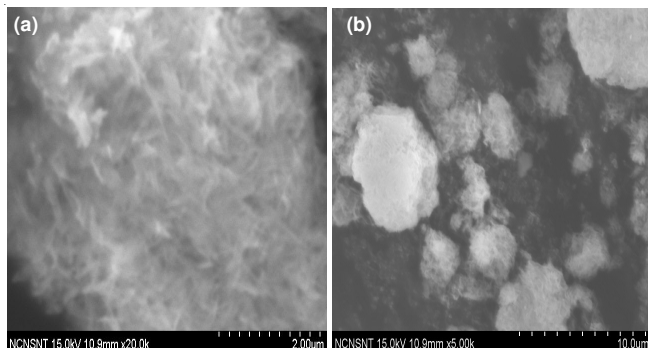


Fig. 3. FESEM image of CuO nanoparticles magnification at 2 and 10 μm

The FESEM analysis for c-CuO clearly shows chain like agglomerated particles as shown in the Fig. 4. Fig. 4a,b FESEM images of carbon functionalized CuO nanoparticles magnification of 2 and 10 μm .

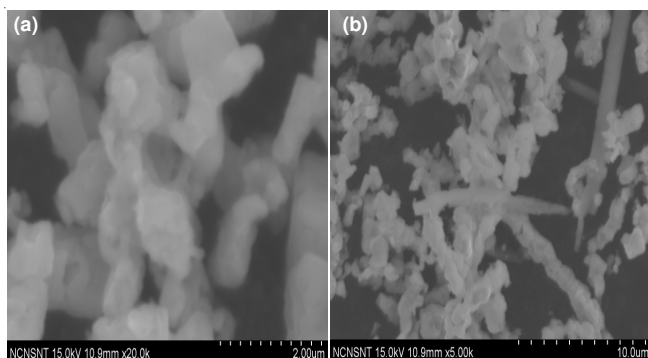


Fig. 4. FESEM image of c-CuO magnification at 2 and 10 μm

Energy dispersive X-ray analysis (EDAX): The CuO nanoparticles were characterized by energy dispersive X-ray analysis. The EDAX spectrum of CuO nanoparticles is given in Fig. 5. Fig. 6 shows the EDAX spectrum of carbon functionalized CuO nanoparticles. Both EDAX spectrum clearly shows the presence of Cu, O and C atoms in CuO and carbon functionalized CuO nanoparticles.

Electrochemical property of bare CuO and c-CuO: The cyclic voltammograms of bare CuO nanoparticles and carbon functionalized CuO nanoparticle in 0.1 M background electrolytes (KOH, NaOH, Na_2SO_4 , H_2SO_4 , HCl, KCl, NaCl, NH_4Cl). In cyclic voltammograms a, b and c represents the electrochemical properties of glassy carbon electrode, bare CuO and c-CuO, respectively.

From Fig.7, it is well observed that in case of 0.1 M H_2SO_4 and HCl shows oxidation peaks for copper ions which are due to the dissolution of CuO nanoparticles. In all the background electrolytes c-CuO showed less current response when compared to that of the bare CuO nanoparticles which might be

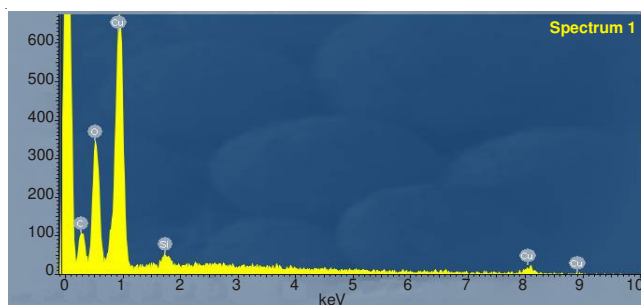


Fig. 5. EDAX analysis of CuO nanoparticles

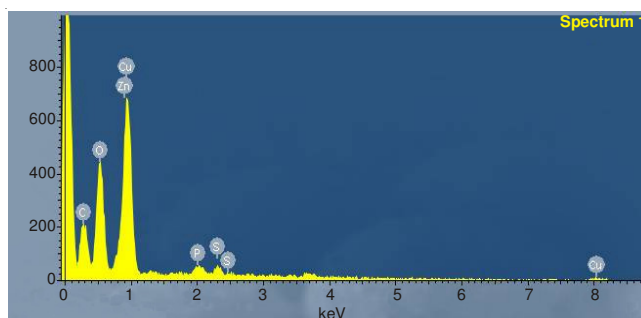
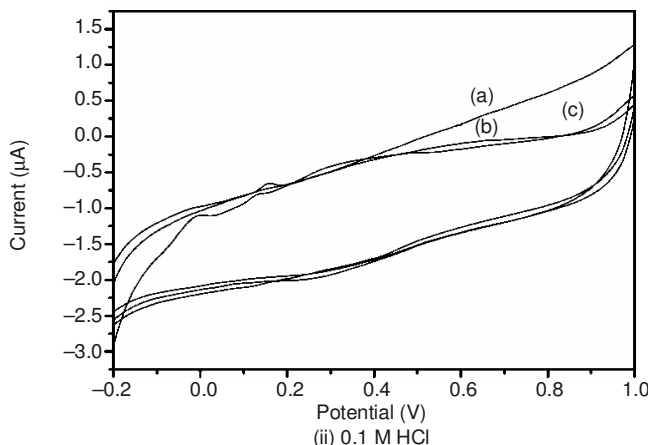
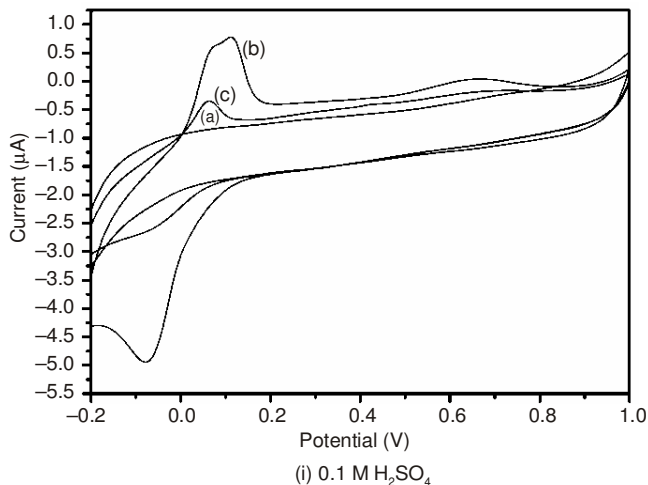


Fig. 6. EDAX analysis of c-CuO

due to the surface group which resides on to it makes it to be less electroactive. From studying the effect of background electrolytes it is clear that in 0.1 M KOH, bare CuO and c-CuO showed higher current response, hence 0.1 M KOH as the background electrolyte.



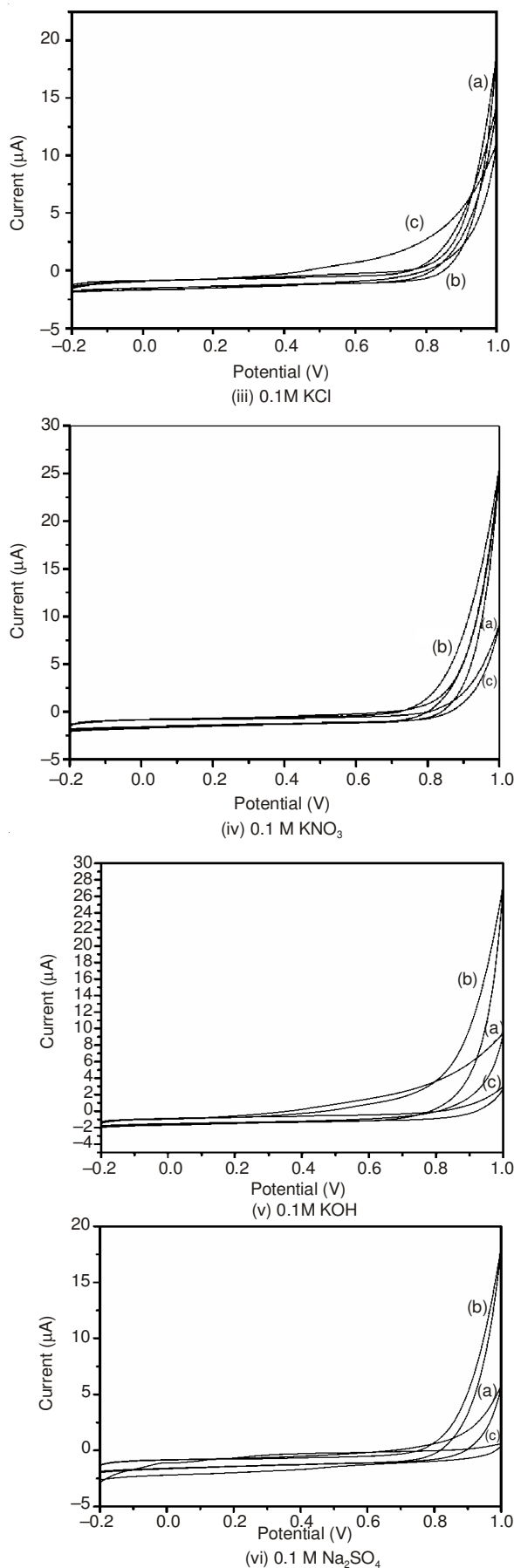


Fig. 7. Cyclic voltammograms of CuO and c-CuO in various backgrounds electrolytes [(a) glassy carbon electrode (b) bare CuO and (c) carbon functionalized CuO on to glassy carbon electrode]

Fig. 8 shows the cyclic voltammogram of 0.1 mM uric acid at bare glassy carbon electrode and bare CuO nanoparticles modified glassy carbon electrode. The cyclic voltammogram of uric acid (curve a) at the bare glassy carbon electrode shows a peak at about 0.6 V as previously reported. It is well known that the oxidation of uric acid at bare glassy carbon electrode is generally believed to be irreversible and requires high over potential. Also, no reproducible electrode response is obtained due to poisoning of the electrode surface by the adsorption of the oxidized product of uric acid. However, the uric acid voltammogram obtained for bare CuO modified glassy carbon electrode showed an oxidation wave with a potential at 0.52 V. From this it is clear that when compared with bare glassy carbon electrode, the c-CuO modified glassy carbon electrode shows shift in potential indicates the electrocatalytic ability of the modified electrode. This electrocatalytic effect was attributed to the larger surface area of the modified electrode. The same was observed in Fig. 9 but the decrease in current response was found due to the surface group that resided on to the CuO nanoparticles. From the electrochemical data it is clear that both the CuO nanoparticles and c-CuO nanoparticles were different due to the surface groups resided on the nanoparticles.

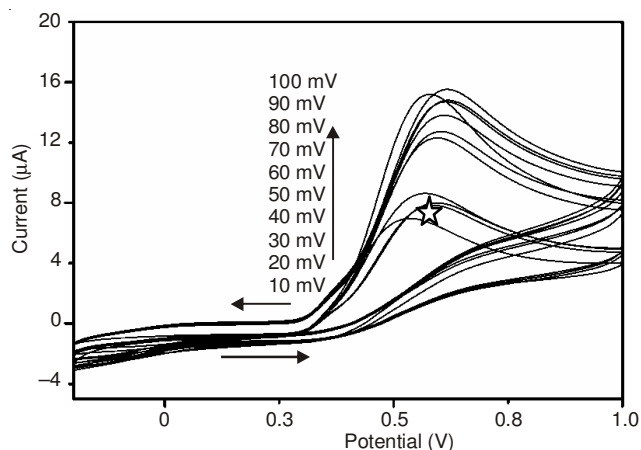


Fig. 8. Cyclic voltammograms of 0.1 mM uric acid in 0.1 M KOH ☆ glassy carbon electrode, bare CuO nanoparticles

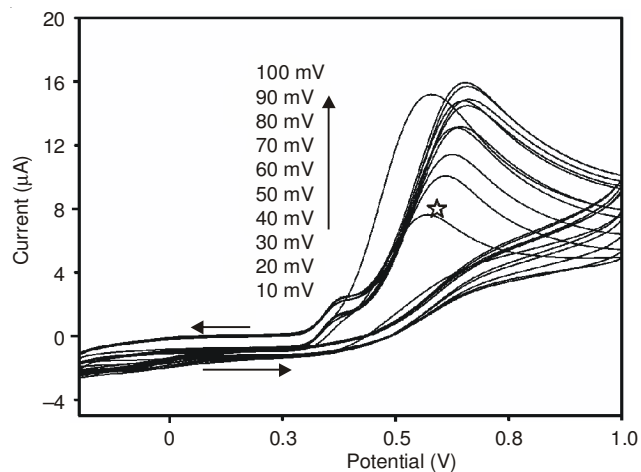


Fig. 9. Cyclic voltammograms of 0.1 mM uric acid in 0.1 M KOH ☆ glassy carbon electrode, c-CuO

Conclusion

Copper(II) oxide and carbon functionalized CuO nanoparticles were successfully synthesized by thermal decomposition method. The synthesized CuO nanoparticles were characterized by various techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy and energy dispersive X-ray analysis (EDAX). The highly porous morphology of CuO nanoparticles were clearly visible in FESEM images. The energy dispersive spectrum gave the elemental composition and it confirms the presence of copper, oxygen and carbon in nanoparticles. The modified glassy carbon electrode was prepared using CuO nanoparticles by drop casting method and these modified electrodes were used to detect the uric acid by cyclic voltammetry. Bare CuO modified electrode shows excellent electrocatalytic ability toward the electrochemical oxidation of uric acid when compared with carbon functionalized CuO nanoparticles and glassy carbon electrode.

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